COMMUNICATIONS

In situ study of the effect of temperature on the electronic structure of $Ni_xMn_{3-x}O_{4+\delta}$ thin films using scanning tunneling spectroscopy

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$Ni_xMn_{3-x}O_{4+\delta}$ $(0.4 \leqslant x \leqslant 1)$ are a series of cubic-spinel-structured material exhibiting a negative temperature coefficient of resistance. The resistance as a function of temperature (T) has been measured from 20 to 200 °C and the data have been fitted to a variable range hopping model in which the resistivity is described as $\rho = \rho_0 T \exp(T_0/T)^{0.5}$ where T_0 was found to be 2.24×10^5 K. Scanning tunneling spectroscopy measurements were carried out over the temperature range of 20–300 °C, to study the shape of the local density of states (LDOS). Such measurements have not been carried out on this class of spinel structured materials before. The distribution of the LDOS around the Fermi level was parabolic in agreement with the model of variable range hopping. The evolution of a peak around 1.8 eV was observed with increasing temperature and found to be completely reversible with temperature. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1505690]

Nickel manganese oxide ($Ni_xMn_{3-x}O_{4+\delta}$ $(0.4 \leqslant x \leqslant 1)$) constitutes a family of cubic spinel structured materials[1] which exhibit negative temperature coefficient (NTC) of resistance characteristics. The dependence of electrical resistance on temperature has made this material useful as temperature sensors mainly as thermistors but more recently these have been used for making infrared detecting bolometers. The electrical conduction process is believed to be due to localized electron hopping from Mn^{3+} to Mn^{4+} in the octahedral sites in the lattice.[2] Different transport models such as nearest-neighbor hopping,[1] variable range hopping,[3] and some empirical models[4,5] have been suggested to explain the conduction of such materials. In developing these models assumptions are made about the possible shape of the distribution of the local density of states (LDOS) around the Fermi level.[6] Although much effort has been devoted into studying the structural, electrical transport, and optical properties[7] of such materials, the electronic structure has remained unresearched. In this work electron tunneling measurements have been carried out using scanning tunneling spectroscopy (STS), in order to elucidate the electronic structure of the material.

Thin films of $Ni_xMn_{3-x}O_{4+\delta}$ were produced using rf magnetron sputtering from a ceramic target, prepared by mixing stoichiometric ratios of NiO and Mn_2O_3, which were pressed into 36 mm diameter disks and subsequently sintered at 1200 °C for 24 h. The target was then cooled to 800 °C and annealed for 40 h before quenching to room temperature[8] to give a well densified monophasic ~3 mm disk.

The films were deposited in a mixed argon/oxygen (12.5% oxygen) ambient on (100) oriented silicon substrates. The films were annealed at 800 °C for 1 h to attain a fully crystallized monophase cubic spinel material, as confirmed using x-ray diffraction (XRD). The microstructures of both the as-deposited and annealed films were examined using scanning tunneling microscopy (STM) which showed dense polycrystalline layers with a well defined grain structure in the annealed state as demonstrated in Fig. 1.

The resistance versus temperature (RT) measurements were undertaken in air from room temperature up to 200 °C in a custom built furnace using a Microcal temperature controller. The resistance was measured using a Kiethley 617 electrometer. STS measurements were carried out in ultrahigh vacuum using an Omicron VT-AFM/STM equipped with an *in situ* sample heater. Tips used for all the measurements were prepared by mechanically sectioning a platinum/iridium wire. The spectroscopy was done at room temperature, 100, 150, 175, 200, and 300 °C. The measurements were carried out on every pixel over an area 600×600 nm^2 area, which was divided into 256×256 pixels. The experimental parameters chosen for the STS measurements were 1 V bias and 0.2 nA tunneling current. In current imaging tunneling spectroscopy (CITS) mode, the I/V curves were recorded simultaneously with a constant current image by the interrupted-feedback-loop technique. Based on these mea-

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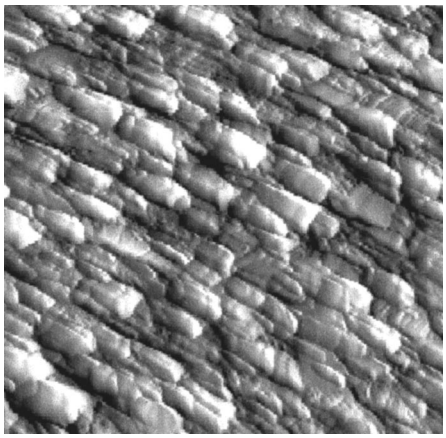

FIG. 1. STM image of a typical annealed film (1200×1200 nm).

surements the first derivative dI/dV was calculated and normalized using the method proposed by Feenstra *et al.*[9] where the differential conductance is divided by the total conductance $[(dI/dV)/(I/V)]$. The divergence problem in this case was overcome by applying some broadening (ΔV) to the I/V values.[10] In all cases ΔV was taken as 1 V. The positions of the spectral features were insensitive to the values chosen for ΔV when the normalization of dI/dV was carried out, although the half width of the peak was reduced at smaller ΔV.

STS measurements have been done over the energy range of ± 3 eV. The results clearly indicate that the shape of the LDOS was parabolic around the Fermi level. With increasing temperature, starting from about 150 °C, a peak evolved in the spectra at around $+1.8$ eV (unoccupied states) indicated in Fig. 2 as SS_2. The appearance of the peak was completely reversible and it disappeared when the temperature was lowered. There were some other features in the occupied part of the spectra as well at higher temperatures although they were not well differentiated. Experiments have been undertaken to rule out any possibility of change in the electronic structure due to oxygen diffusing out at elevated temperature in high vacuum inside the microscope. Two films were subjected to the same heating cycle, as used in the STS studies, one in an oxygen rich atmosphere and the second in air. Spectroscopy was then carried out on both sets of samples but the results were similar to the original ones. A further small feature can also be seen in the spectra very near to the Fermi level indicated as SS_1 in Fig. 2, but is not well resolved in the wide energy range over which the spectroscopy was carried out.

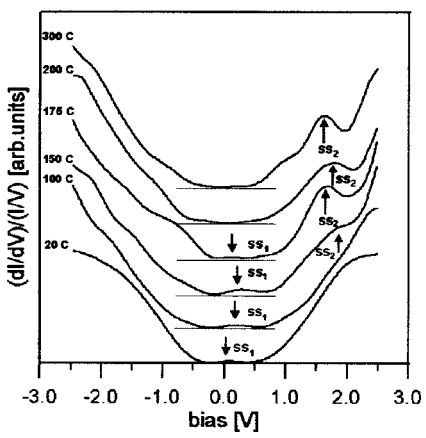

FIG. 2. Representative STS spectra at different temperatures.

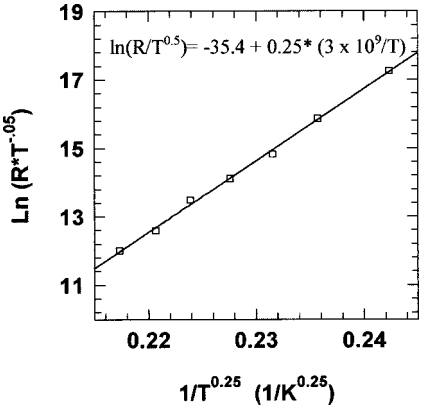

FIG. 3. RT data fitted to Mott model.

The resistivity of the film was found to be 327 Ω cm at 50 °C. The RT data could be fitted to the variable range hopping model proposed by Mott[11] which assumes that the LDOS around the Fermi level is constant with energy and the resistivity is described by

$$\rho = \rho_0 T^{0.5} \exp(T_0/T)^{0.25}, \tag{1}$$

where $T_0 = \beta/k_b g(\mu) a_0^3$, where $\beta = 21.2 \pm 1.2$ is a numerical factor which is determined by solving the appropriate percolation problem,[12] k_b is the Boltzmann constant, $g(\mu)$ is the density of states, and a_0 is the Bohr radius. A plot of $\ln(RT^{-0.5})$ vs $T^{-0.25}$ is shown in Fig. 3 and implies an excellent fit to Eq. (1). However the slope gives an unfeasibly large value of $T_0 = 3 \times 10^9$ K, implying a very low density of states at the Fermi level, $g(\mu) = 5.5 \times 10^{20}$ cm^{-3} eV^{-1}, taking a_0 to be the Bohr radius of the hydrogen atom.

The data could also be fitted to the modified model of variable range hopping proposed by Shklovskii and Efros[6] based on the assumption of a parabolic LDOS around the Fermi level. The resistivity in this model is given by

$$\rho = \rho_0 T \exp(T_0/T)^{0.5}, \tag{2}$$

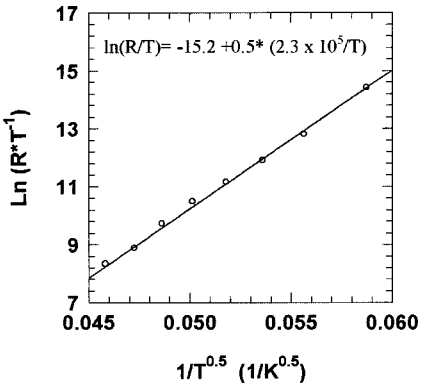

FIG. 4. RT data fitted to Shklovskii and Efros model.

where $T_0=\beta_1 e^2/k_b\kappa a_0$ where $\beta_1=2.8$ is a numerical factor,[6] e is the charge on an electron, k_b is Boltzmann constant, κ describes the Coulomb interaction between the electrons, and a_0 is the Bohr radius. Here, $\kappa=\varepsilon_0\varepsilon_r 4\pi$, where ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material. The product $a_0^*\ \varepsilon_r$ gives the effective radius of an atom of the material. A plot of $\ln(RT^{-1})$ vs $T^{-0.5}$ is shown in Fig. 4 and as for the Mott model the data appear to be very consistent with Eq. (2), although in this case the slope yields a more reasonable value of $T_0=2.3\times10^5$ K. The corresponding value for the effective radius of 2.1×10^{-10} m is quite realistic, suggesting that this model is more consistent with the data.

It is evident from Figs. 3 and 4 that the conduction mechanisms in this material cannot be elucidated from RT measurements alone [i.e., both Eqs. (1) and (2) provide statistically good fits to the data]. However, the STS measurements, which show that the distribution of the LDOS around the Fermi level to be parabolic, do not support the Mott model [Eq. (1)] for transport in nickel manganate. Other features observed in the spectra are at quite high energy and are probably not the states, which take part in the conduction in this material. Presently, work is being carried out to study the LDOS in the low energy region (±0.5 eV). This would be an opportunity to study the electronic states close to the Fermi level, which are thought to be responsible for the conduction process.

In conclusion the distribution of the LDOS in thin sputtered films of cubic spinel $Ni_xMn_{3-x}O_{4+\delta}$ was found to be parabolic with energy. STS measurements were undertaken in a spinel structured material. It is also emphasized that the spectra were recorded in the temperature range where this material is most commonly used. The STS observations are consistent with the modified variable range hopping model for conductivity developed by Shklovskii and Efros. They would appear to exclude Mott variable range hopping in this material.

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